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Ion Elutriation of Silver and Free Cyanide From Wastewater

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Ion Elutriation of Silver and Free Cyanide From Wastewater

By F. H. Nehl, D. Tom, and G. B. Atkinson

UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES
Rhea Lydia Graham, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cc/min	cubic centimeter	L/h	liter per hour
	per minute	M	molar
diam	diameter	mg/L	milligram per liter
g	gram	min	minute
g/L	gram per liter	mL	milliliter
h	hour	mL/min	milliliter per minute
in	inch	pct	percent
L	liter	ppm	part per million
lb	pound	vol/h	volume per hour

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ION ELUTRIATION OF SILVER AND FREE CYANIDE FROM WASTEWATER

By F. H. Nehl,¹ D. Tom,² and G. B. Atkinson³

ABSTRACT

Ion elutriation was used to extract silver cyanide complexes and free cyanide from aqueous streams containing up to 10 ppm silver and 5 ppm free cyanide. Screening tests selected nine of 350 different surfactants for further, larger scale experiments. The screening procedure used 0.1 g of each of the surfactants in 300 mL of synthetic wastewater. Air was sparged into the test cell at 50 cc/min. The foam was refluxed during the tests and was not sampled. Samples of the solution were taken at specified intervals and analyzed by wet chemical methods for free cyanide and by atomic absorption for silver content. The most effective surfactants lowered the silver and free cyanide concentrations to less than 0.5 ppm in 1 h or less. These surfactants were quaternary amine salts with one long chain (C12-C18) organic group and three methyl groups. Experiments using 3 L batches of wastewater or an ion elutriation cell continuously fed with solution draining from an inactive heap leach operation confirmed the results from the screening tests.

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INTRODUCTION

Ion elutriation, also known as ion flotation, was first proposed by Sebba in 1962 as a method to remove and concentrate ions from dilute solution (1)⁴, typically approximately 10 ppm. It has not been used commercially to a great extent (2-3), but has been studied in the laboratory (4-5) as a method of concentrating anionic or cationic species. Ion elutriation holds the promise that selection of the right surfactant will make selective removal and concentration of many different species possible.

The technique is illustrated in figure 1. A surfactant is added to an aqueous stream. One end of the surfactant molecule is electrically charged and is attached to a long, hydrophobic, organic tail. The polarity of the charged end is selected to be opposite the polarity of the ion to be extracted from the aqueous stream. Electrostatic attraction between the charged end of the surfactant and the aqueous ion result in the formation of an ion-surfactant pair. Air is bubbled through the stream containing the ion-surfactant pair and the hydrophobic tail of the ion-surfactant pair attaches to a rising air bubble. These rising air bubbles take the ion-surfactant pair to the surface generating an easily removed foam. The removed foam is collapsed, yielding a product concentrated in the extracted ion that is suitable for further processing.

Waters containing cyanide from precious metals mining operations were attractive candidates for ion elutriation. Although any water exiting the mining site can be chemically treated to destroy the contained cyanide, it might be preferable to extract such contained cyanide and recycle it to the mining operation. Such extraction and recycle would lessen the need to buy additional cyanide and would eliminate the need to buy the chemical oxidizers necessary to destroy the cyanide in solution. Such cyanide extraction could be accomplished using ion elutriation with the proper surfactant. Recycle of the extracted cyanide would require development of a scheme to separate the surfactant from the cyanide, an issue not addressed here. The water treated with ion elutriation could then meet the Federal drinking water standard for cyanide content, which is <0.23 ppm (6).

EXPERIMENTAL CONDITIONS

Three different ion elutriation cells were built. Two were batch fed with working volumes of 300 mL and 3 L, respectively. The third cell was continuously fed with a working volume of 300 mL. Diagrams of the two cell types are shown in figure 2.

Screening experiments used the batch fed 300 mL cell. This cell was made of 1-1/2-in clear PVC pipe 12-in long. The bottom of the pipe was closed with a blank PVC flange equipped with a glass frit. The top of the cell was fitted with a stainless steel screen treated with Dow silicone anti-foam agent that served as a foam breaker. A sampling port with a rubber septum was tapped into the side of the cell. Air was bubbled through the frit at 50 cc/min and 10 mL samples of the solution were taken periodically. Each experiment lasted 60 min and the samples taken were analyzed for silver and free cyanide concentration.

A second batch fed cell was constructed in a similar manner but was made from 4-in clear PVC pipe to give a working volume of 3 L. It was equipped with a vacuum foam collection system instead of a stainless steel screen foam breaker. This cell was used to study the effects of varying surfactant concentrations and air flow rates.

⁴Italic numbers in parentheses refer to items in the list of references at the end of this report.

A continuously fed cell was also built. The materials of construction were the same as those used for the 300 mL batch cell. This cell was equipped with an upper solution feed port and pump and a lower solution discharge port. The discharge port was equipped with an overflow that assured solution feed and discharge rates were balanced. Foam was vacuumed off continuously into a glass Erlenmeyer flask.

The extraction in each experiment was calculated from the analyses and volumes of three different solution streams. The solution entering the ion elutriation cell is called the cell feed or, more simply, feed solution. The foam generated in the cell has the air removed and is called collapsed foam. Treated solution exiting the cell through the discharge weir is called discharge solution.

Silver analyses were done by atomic absorption. Free cyanide was determined by ion chromatography using a Dionex 4500 machine. The starting solution averaged 9 to 10 ppm silver and 5 ppm free cyanide. Surfactants were obtained from 69 different manufacturers. Also tested were household detergents and cleaners.

PROCEDURE

The 300-mL batch cell was used for the screening tests. A stock cyanide solution containing 300 ppm Ag was prepared from AgCN and an equimolar amount of NaCN to form the soluble silver species $\text{Ag}(\text{CN})_2^-$. Ten milliliters of this stock solution was diluted with water to 300 mL to produce a 10-ppm Ag cell feed solution. One-tenth gram of the surfactant to be tested was added to the 300 mL of feed solution and the solution was stirred for 15 min. This 0.1 g of surfactant in 300 mL produced a solution containing 333 ppm of the surfactant. Surfactant was added to the feed solution as it came from the supplier as either liquid or solid. Surfactants not readily soluble in the feed solution were first dissolved in 5 to 20 mL of 100 pct ethyl alcohol (EtOH), heated if needed, and then added.

After the feed solution and dissolved surfactant had been stirred for 15 min, a 10 mL head sample was taken. The remaining feed solution was added to the 300 mL batch cell with air flowing at 50 cc/min. Ten- milliliter solution samples were taken after 5, 10, 20, 30, and 60 min. Foam generated during these tests rose to collapse at the stainless steel foam breaker. The solution from this collapsed foam ran back into the cell.

The effect of different air flow rates and surfactant concentrations were investigated using the batch 3 L cell. Three liters of feed solution were prepared as described for the 300 mL screening cell. The required weight of surfactant (0.2, 0.5, or 1.0 g) was dissolved in EtOH, added to the feed solution, and stirred for 15 min. This feed solution was added to the 3-L cell with air flowing at 200, 500, or 800 cc/min. Solution samples were taken as with the screening cell. The foam generated was removed by vacuum from the top of the cell and collected in a glass flask. The experiment was stopped after 1 h and the volumes of collapsed foam and of solution remaining in the cell were measured.

The continuously fed cell was used to evaluate ion elutriation of cyanide from an actual heap drainage solution obtained from the inactive Trinity silver mine in central Nevada. Solution draining from one of these ore heaps was obtained as an example of an actual solution that contained cyanide. The heap drainage solution was diluted 50 or 100:1 and used as cell feed. The solution was diluted to bring the concentration of silver and cyanide down to levels that could be treated by ion elutriation. Such dilution was done only to allow gathering of experimental data and probably would not be an actual waste treatment scheme. One-hundred milliliters of 0.06M surfactant solution in EtOH was freshly prepared for each test.

Cyanide and silver extraction as a function of the residence time of solution in the cell was investigated using the continuously fed 300 mL cell. Residence time was controlled by the feed rate. Feed rates of 900, 1,800, and 2,700 mL/h were used. A feed rate of 300 mL/h had a 1-h residence time, a feed rate of 900 mL/h had a 20-min residence time, a feed rate of 1,800 mL/h had a 10-min residence time, and a feed rate of 2,700 mL/h had a 7-min residence time. Experiments using the 300 mL cell began by adding 3 mL of the EtOH surfactant solution to 300 mL of 100:1 diluted Trinity heap drainage. A 10-mL head sample was taken after 10 min of stirring. The solution was stirred for an additional 5 min, sampled, and added to the elutriation cell. Air flow was set at 50 cc/min and feed and surfactant pumps were started. Solution volume in the cell was held at 300 mL by the overflow weir which allowed discharge solution to overflow at the same rate feed solution entered the cell. Discharge solution was captured and the volume monitored. Foam was suctioned off by a vacuum tube suspended 1-1/2 to 2 in from the top of the foam. This was necessary because the foam produced was fragile and tended to collapse as it travelled up the cell.

Overflow sampling was started when one cell volume of feed solution had passed through the cell. With a feed rate of 900 mL/h, overflow sampling was started after 20 min, and samples were taken at 40 and 60 min. At 1,800 mL/h, the first sample was taken at 10 min with remaining samples collected at 20, 40, and 60 min. Finally, at 2,700 mL/h, sampling started after 7 min and samples were collected at 21, 35, and 49 min. Discharge solution flow was measured when the samples were taken. The collapsed foam volume was measured and recorded.

RESULTS AND DISCUSSION

The screening experiments found 45 surfactants that extracted silver cyanide complexes and 38 surfactants that extracted free cyanide of 350 surfactants tested. Extraction was measured by analyzing the solution samples for silver and free cyanide over the course of the experiment. The extraction rate was calculated from the slope of a straight line fitted to the time versus concentration data.

A typical example of the curve fitting and slope calculation can be seen in figure 3. The surfactant used was Arquad 16/50, available from Akzo. Figure 3 shows that the feed solution contained 9.4 mg/L silver as the cyanide complex and 3.5 mg/L free cyanide. The concentration of both silver and free cyanide decreased after 60 min of foam production. Silver concentration fell from 9.4 to 0.07 mg/L, and free cyanide concentration fell from 3.5 to 0.17 mg/L. A straight line was fitted to the data points and the slope calculated as a measure of extraction. The slope for the silver data was -0.15 ppm/min, and for the free cyanide data was -0.05 ppm/min. The more negative such a slope is the greater the rate of extraction.

In comparison, figure 4 shows the time versus concentration data for Henkel's Alamine 336. The slope for the silver data was -0.06 ppm/min and the slope for the free cyanide data was -0.04 ppm/min. Since the slopes calculated from the Alamine 336 data are less negative than the slopes calculated from the Arquad 16/50 data, the Arquad 16/50 extracts silver and free cyanide more rapidly than does Alamine 336.

At the conclusion of the screening tests all the surfactants were ranked according to the slopes calculated from the extraction data. Nine surfactants with the most negative slopes were selected for further experiments. These surfactants are listed in table 1. These nine surfactants were used in further, larger scale experiments using the batch fed 3-L cell.

Table 1.—Most effective surfactants

Manufacturer	Common name	Chemical name
Akzo	Arquad 16/50	Trimethylhexadecyl ammonium chloride
Akzo	Arquad C-50	Trimethylcoco ammonium chloride
Akzo	Arquad T-50	Trimethyltallow ammonium chloride
Aldrich . . .	28,531-5	Cetylpyridinium bromide, monohydrate
Aldrich . . .	85,582-0	Cetyltrimethyl ammonium bromide
Aldrich . . .	86,042-5	Myristiltrimethyl ammonium bromide
Sigma	B-8879	Benzethonium chloride
Sigma	M-7379	Methylbenzethonium chloride
Sigma	M-7635	Mixed alkyltrimethyl ammonium bromide

Table 2.—Silver and cyanide extractions in 3L batch tests

Manufacturer	Surfactant	Air, cc/min	Weight, g	Ag extracted, pct	CN extracted, pct	Solution remaining, pct
Akzo . . .	Arquad 16/50.	200	0.10	20.03	2.64	98.1
			1.00	47.98	52.84	98.7
		500	0.50	94.30	97.06	95.1
		800	0.10	35.87	21.97	99.3
			1.00	99.70	96.76	31.3
Aldrich . .	28,531-5.	200	0.10	16.96	5.92	97.4
			1.00	18.15	13.30	97.0
		500	0.50	99.27	98.55	82.0
		800	0.10	45.84	8.07	90.9
			1.00	99.74	98.51	52.4
Sigma . . .	B-8879.	200	0.10	0.00	0.00	>99.9
			1.00	0.00	0.00	<99.9
		500	0.50	75.49	54.55	91.6
		800	0.10	0.00	0.00	>99.9
			1.00	99.56	96.81	63.0

Typical results from the experiments using the 3-L batch fed cell are tabulated in table 2. Air flows of 200 cc/min and surfactant weights of 0.1 g extracted little of the silver or free cyanide and left most of the solution in the ion elutriation cell. Increasing air flow and weight of surfactant increased the extraction of silver and free cyanide and decreased the solution volume remaining

in the cell. As an example, the data from the Akzo Arquad 16/50 3-L batch experiments have been graphed in figures 5-7. Figure 5 shows the percent of silver and free cyanide extracted and the percent of solution remaining when 0.1 g of Arquad 16/50 was added and air flow was 200, 500, or 800 cc/min. The feed solution contained 10 ppm silver and 5 ppm free cyanide. Extraction of silver or free cyanide did not exceed 40 pct at each air flow. More than 99 pct of the feed solution remained in the cell for each of the experiments.

Figure 6 shows the experimental results when 0.5 g of the surfactant is used. At 200 cc/min air flow, extraction of silver and free cyanide remains below 40 pct. Extraction increased at the 500 and 800 cc/min air flows. At 500 cc/min air flow, 95 pct of both the silver and free cyanide have been extracted from the feed solution. Ninety-five percent of the solution remained in the cell. Increasing the air flow to 800 cc/min slightly increased extraction of both silver and free cyanide but left less than 80 pct of the feed solution in the cell.

A third set of experimental conditions using 1 g of surfactant is presented in figure 7. When an air flow of 200 cc/min is used, extractions are low and most of the solution remains in the cell. Increasing the air flow to 800 cc/min extracts most of the silver and free cyanide but less than 80 pct of the solution remains in the cell. Optimum operation occurs at an air flow of 500 cc/min. Most of the silver and free cyanide are extracted to the foam and most of the feed solution remains in the cell.

Among the experimental conditions presented in figures 5-7, the best balance between the most extraction of silver and free cyanide and most solution retention occurred with 0.5 g of the Arquad 16/50 with air flow at 500 cc/min. Less surfactant decreased solution carry over, but extraction rates of both silver and free cyanide fell to as low as 3 pct. More surfactant increased the extraction only marginally. Increasing the air flow to 800 cc/min increased silver and free cyanide extractions by 1 or 2 pct, but the amount of solution remaining in the cell fell from 95 to 75 pct. Table 2 shows that this occurred with all the surfactants tested. This is not surprising since the surfactants tested have similar structures and molecular weights.

As a final test of the usefulness of ion elutriation, the technique was used to remove silver and free cyanide from drainage from heaps at an inactive silver heap leach operation. The drainage solution contained 30 mg/L silver and 500 mg/L free cyanide. This solution was diluted 100:1 to make a suitably dilute feed for ion elutriation. A 300 mL ion elutriation cell was used at feed rates of 300, 900, or 1,800 mL/h. Each of the nine previously mentioned surfactants was used with the experimental results summarized in table 3.

An overall extraction was calculated for each surfactant by adding the percent silver extracted, the percent free cyanide extracted, and the percent of the solution remaining in the cell and dividing by 3. Sigma Chemical's M-7365 turned out to be the best surfactant for a solution feed rate of 300 mL/h. Sigma M-7365 extracted 76 pct of the silver, 91 pct of the free cyanide, and left 94 pct of the feed solution in the cell for an overall extraction of 87.1 pct. Arquad 16/50 did almost as well with an overall extraction of 83.3 pct. The main advantage in the use of Arquad would be cost. The Sigma chemical is a research reagent and relatively expensive. Akzo's Arquad 16/50 is a commodity chemical available in bulk quantities relatively cheaply (<\$2.00/lb).

Increasing the cell feed rate to 900 mL/h decreased the overall extraction for all the surfactants. Arquad T-50 showed the highest overall extraction for an ion elutriation cell fed at 900 mL/h with an overall extraction of 58.8 pct. Increasing the feed rate to 1,800 mL/h lowered the overall extraction further. Arquad T-50 had the highest overall extraction, 51.3 pct. All the other surfactants used did not exceed a 50 pct overall extraction. Of the few surfactants tested with a solution feed rate of 2,700 mL/h, silver extractions

Table 3.—Effect of feed rate on overall extraction in continuously fed 300 mL cell, percent

	Feed rate, mL/h		
	300	900	1,800
Arquad 16/50	83.3	38.1	37.4
Arquad C-50	67.1	43.8	40.1
Arquad T-50	62.0	58.8	51.3
Aldrich 28,531-5	79.7	38.2	40.0
Aldrich 85,582-0	78.7	36.0	46.5
Aldrich 86,042-5	72.7	39.3	35.4
Sigma B-8879	66.9	33.6	40.7
Sigma M-7379	70.2	38.8	35.8
Sigma M-7635	87.1	39.2	34.4

Table 4.—Average extractions from three experiments for different feed dilutions in a continuously fed 300 mL cell, percent

Surfactant	Dilution	
	100:1	50:1
Arquad 16/50	83.3	85.9
Arquad C-50	67.1	84.4
Arquad T-50	67.0	84.7
Aldrich 28,531-5	79.7	90.4
Aldrich 85,582-0	78.7	90.2
Aldrich 86,042-5	77.7	94.8
Sigma B-8879	66.9	85.0
Sigma M-7379	70.2	85.2
Sigma M-7635	87.1	95.3

were less than 1 pct, free cyanide extractions were less than 5 pct, and more than 99 pct of the solution remained. The poor extraction of silver and free cyanide showed that little ion elutriation was occurring in a cell fed at 2,700 mL/h.

Data generated using laboratory generated feed solution to the ion elutriation cell showed that the more concentrated the feed, the better the extraction. To see if this held true with the diluted heap leach solution, a 50:1 dilution was used instead of the 100:1 solution previously used and fed to the cell at 300 mL/h. The results are in table 4. Sigma M-7635 becomes the best surfactant in this group, just as it was for the cell fed at 300 mL/h with 100:1 diluted water.

As expected, extractions became larger with the 50:1 feed. M-7635 fed 100:1 feed extracted 76.3 pct of the silver, 90.9 pct of the free cyanide, and left 93.9 pct of the entering solution for an overall extraction of 87.1 pct. With the feed solution being the more concentrated 50:1 dilution, 89.5 pct of the silver was extracted, 97.5 of the free cyanide was extracted, and 99.0 pct of the solution was left for an overall extraction of 95.3 pct.

CONCLUSIONS

Screening tests to determine if an effective ion-elutriation surfactant for silver and free cyanide could be found revealed that there are surfactants that can remove both these species from solution to less than 0.5 ppm in 1 h or less. Further experiments using the most promising surfactants were conducted on a larger scale and in continuously fed cells. These experiments showed that the most effective combination of surfactant concentration and air flow rate could extract 95 pct of both silver and free cyanide while 95 pct of the feed solution emerged from the cell as purified discharge solution. When this technique was applied to diluted heap leach drainage waters, the technique remained effective within certain feed solution flow rates. Depending on the initial concentration of the solution fed to an ion elutriation cell, the technique can lower silver and cyanide concentrations to near or below regulatory limits.

REFERENCES

1. Sebba, F. Ion Flotation. Elsevier, 1962, 154 pp.
2. Jdid, E., P. Blazy, J. Bessieue, and R. Durand. Removal of Cadmium Contained in Industrial Phosphoric Acid Using the Ionic Flotation Technique. Paper in Trace Metal Removal from Aqueous Solution, ed. by R. Thompson, Royal Society of Chemistry, London, 1986, pp. 111-112.
3. Pinfold, T. A. Ion Flotation. Ch. in Adsorptive Bubble Separation Techniques, ed. by Robert Lemlich. Academic Press, 1972, pp. 53-73.
4. Grieves, R. B., W. Salowiak, and D. Bhattacharyya. Foam Fractionation Selectivity Sequences of Quaternary Ammonium Surfactants for Simple and Complex Anions: A Review. Ch. in Recent Developments in Separation Science, ed. by Norman N. Li. CRC Press, v. 5, 1979, pp. 55-65.
5. Rubin, Alan J. Removal and Use of Hydrolyzable Metals in Foam Separations. Ch. in Adsorptive Bubble Separation Technology, ed. by R. Lemlich, Academic Press, NY, 1993, pp. 199-217.
6. Ciriello, S., S. M. Baunett, and F. J. Deluise. Removal of Heavy Metals From Aqueous Solutions Using Microgas Dispersions. Separation Sci. and Technol., v. 17, No. 4, 1982, p. 522.

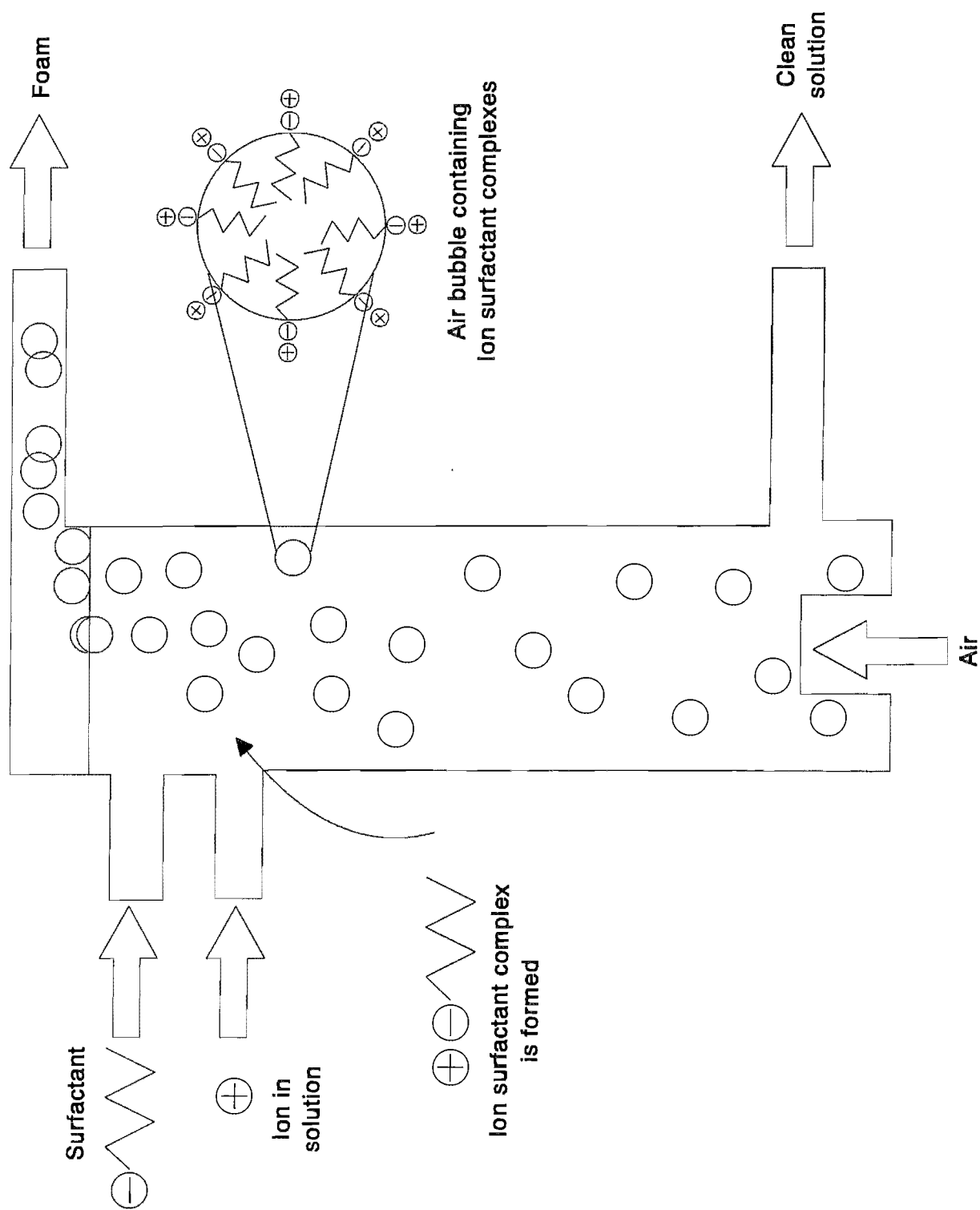


Figure 1
Ion elutriation schematic.

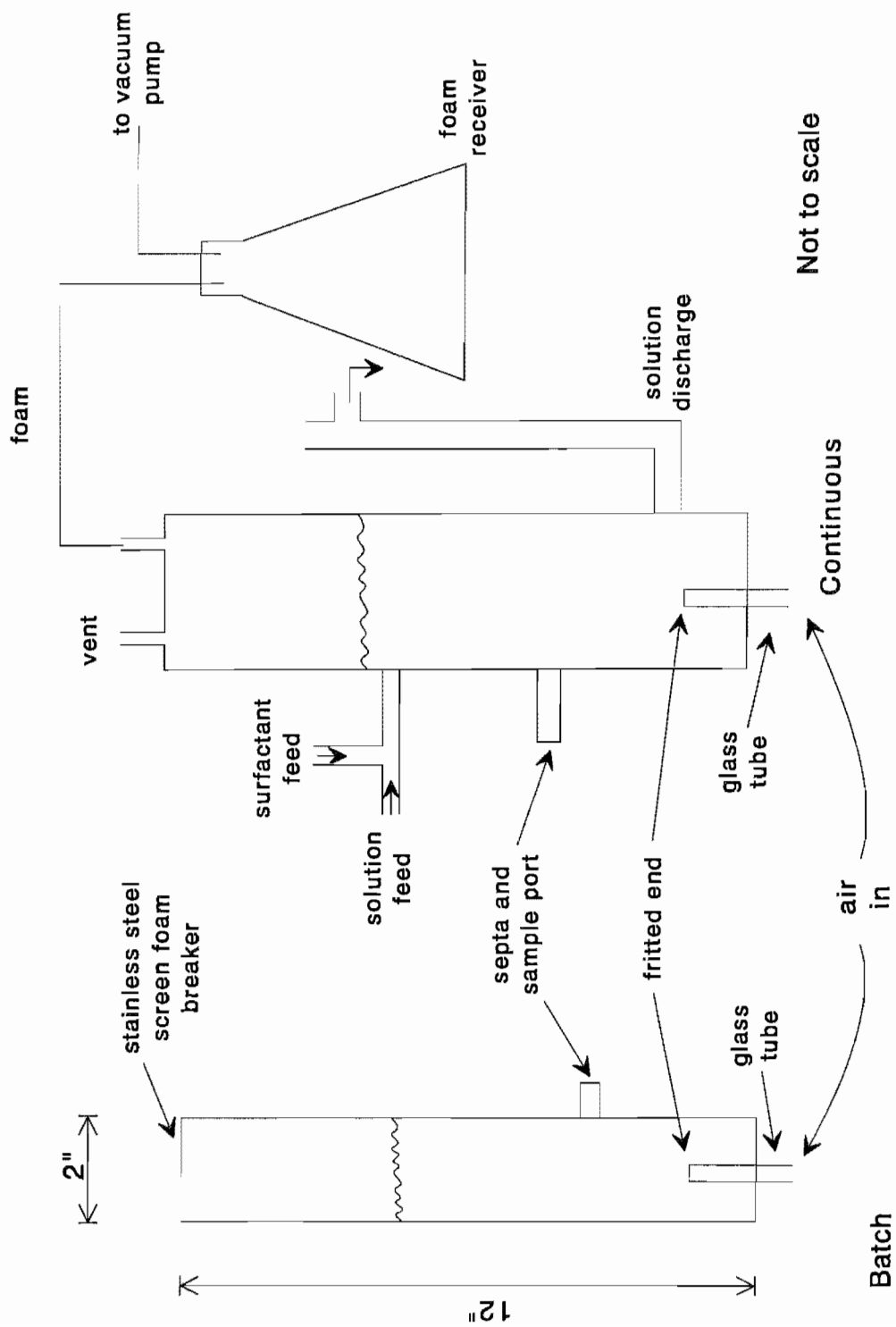


Figure 2
Typical ion elutriation cells.

Arquad 16/50

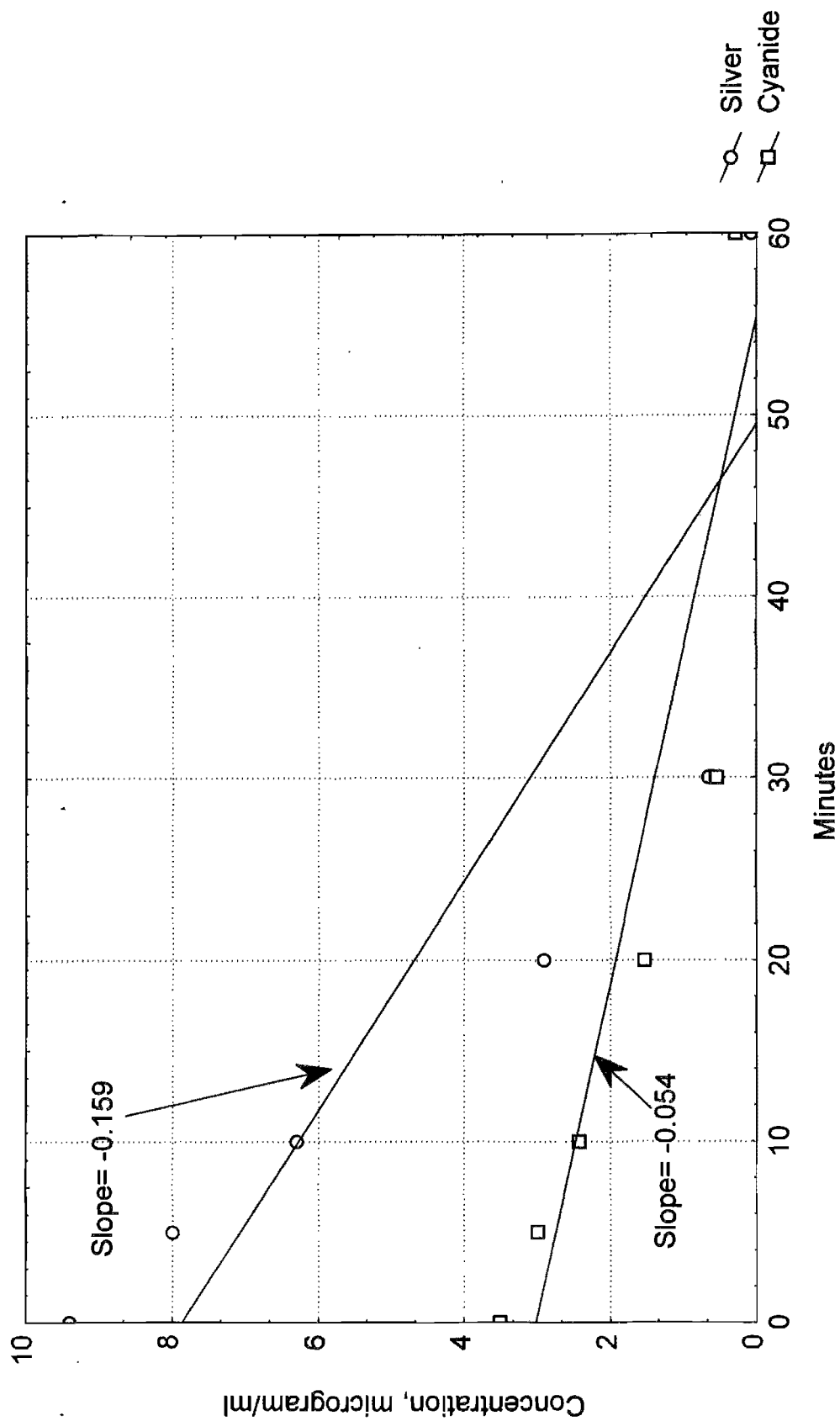


Figure 3
Screening experiment showing good extraction, 300 mL batch cell.

Alamine 336

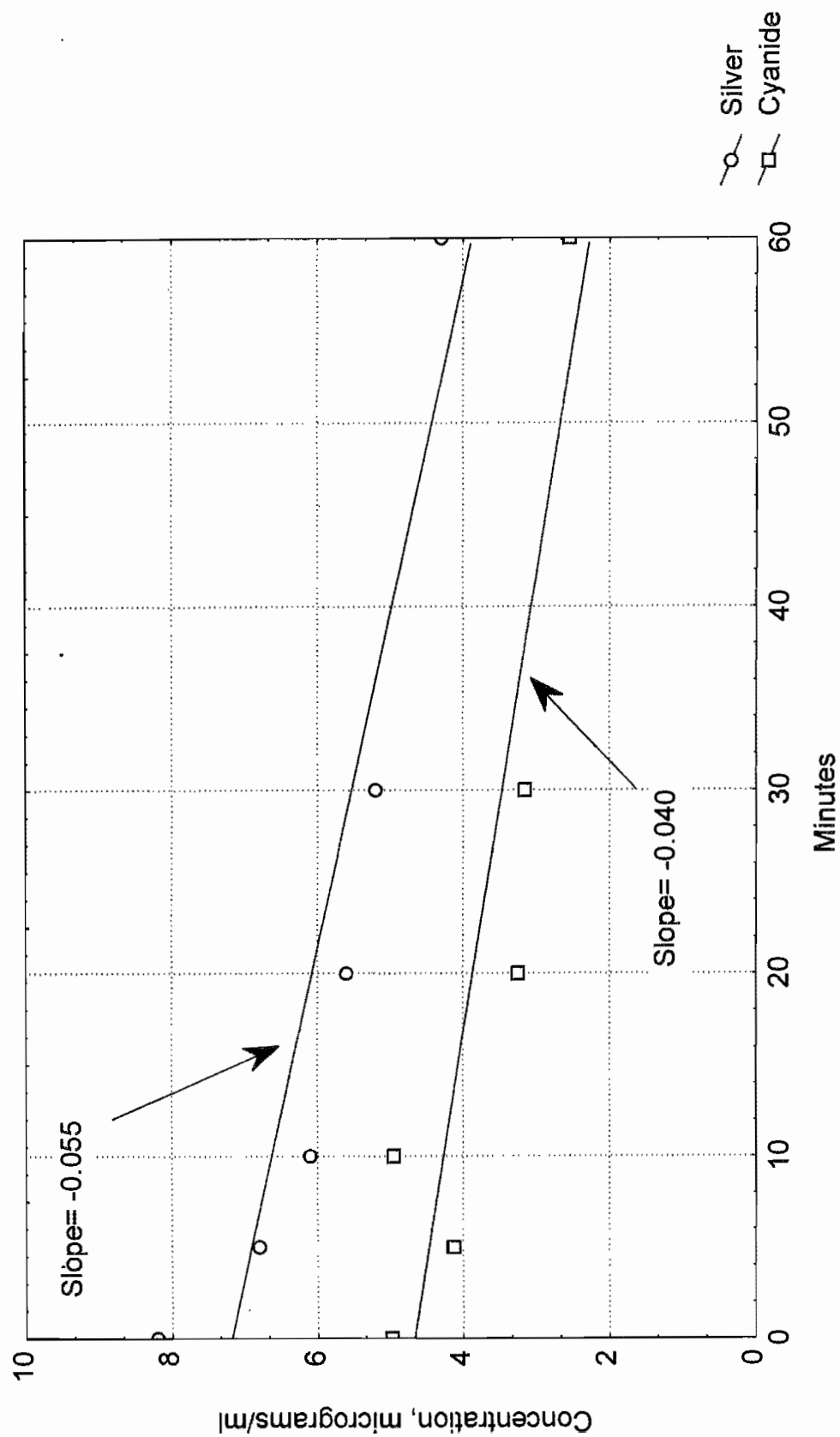


Figure 4
Screening experiment showing poor extraction, 300 mL batch cell.

Arquad 16/50

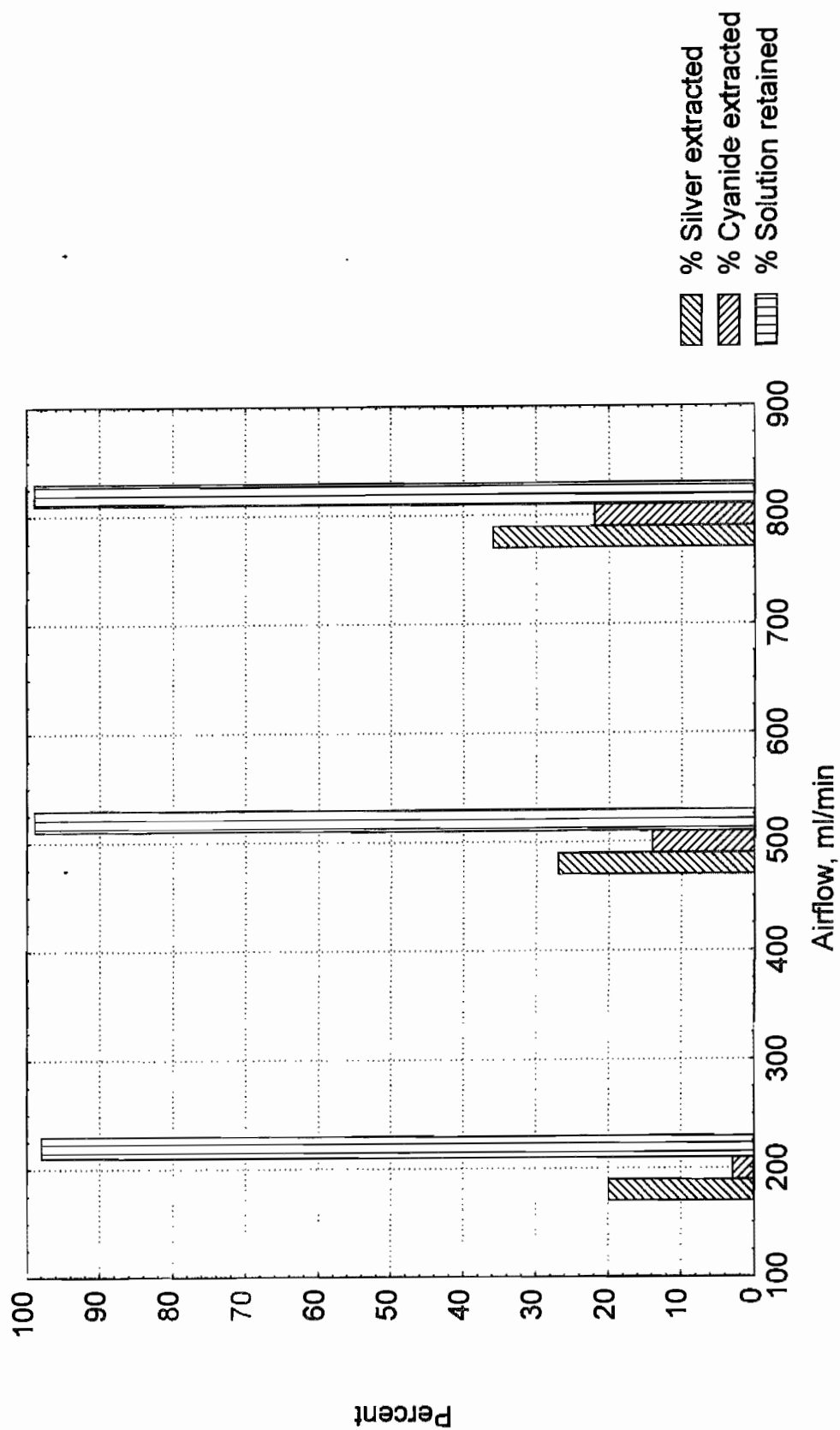


Figure 5
Effect of air flow on extraction, 0.1 g surfactant, 3 L batch cell.

Arquad 16/50

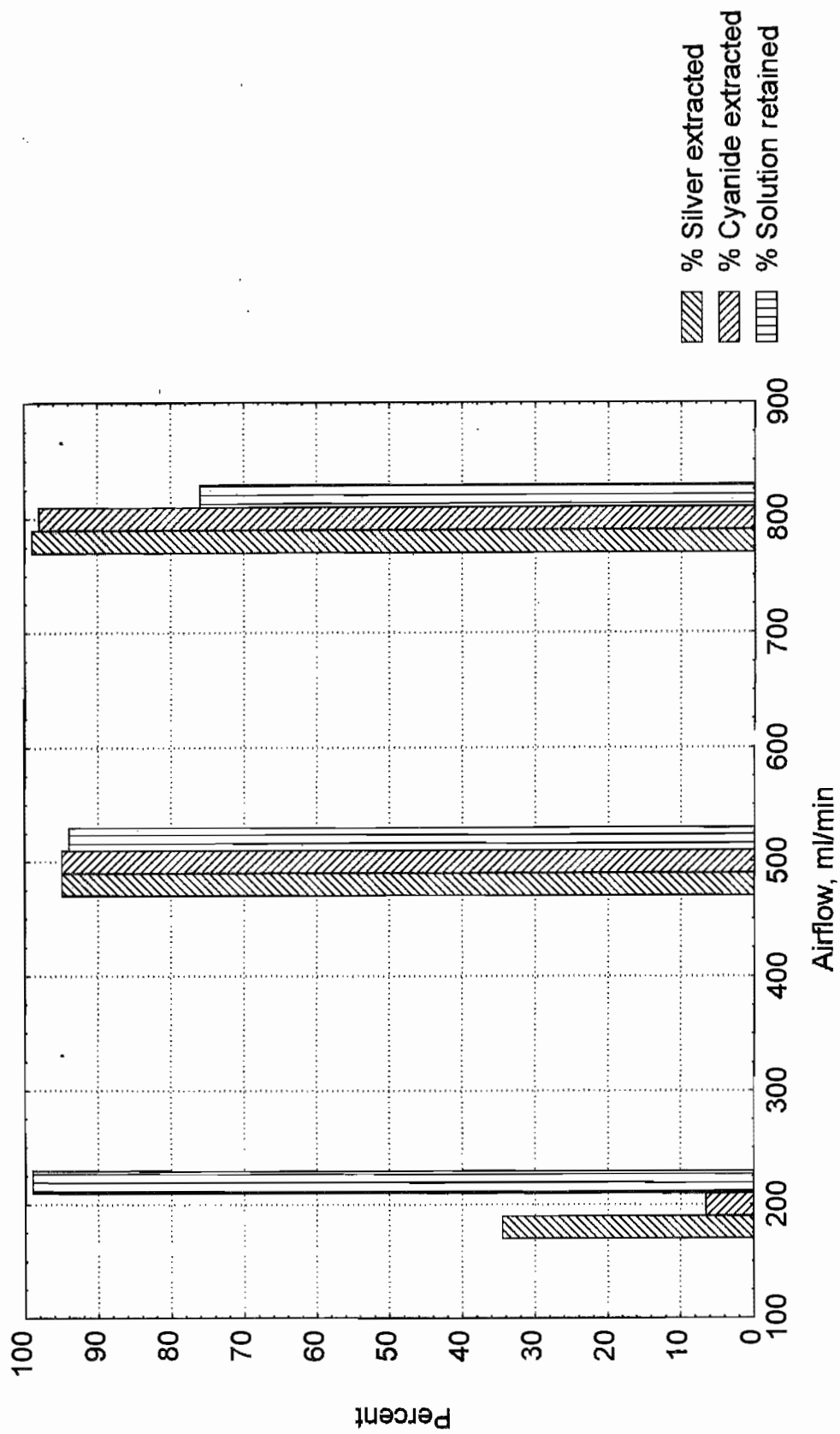


Figure 6
Effect of air flow on extraction, 0.5 g surfactant, 3 L batch cell.

Arquad 16/50

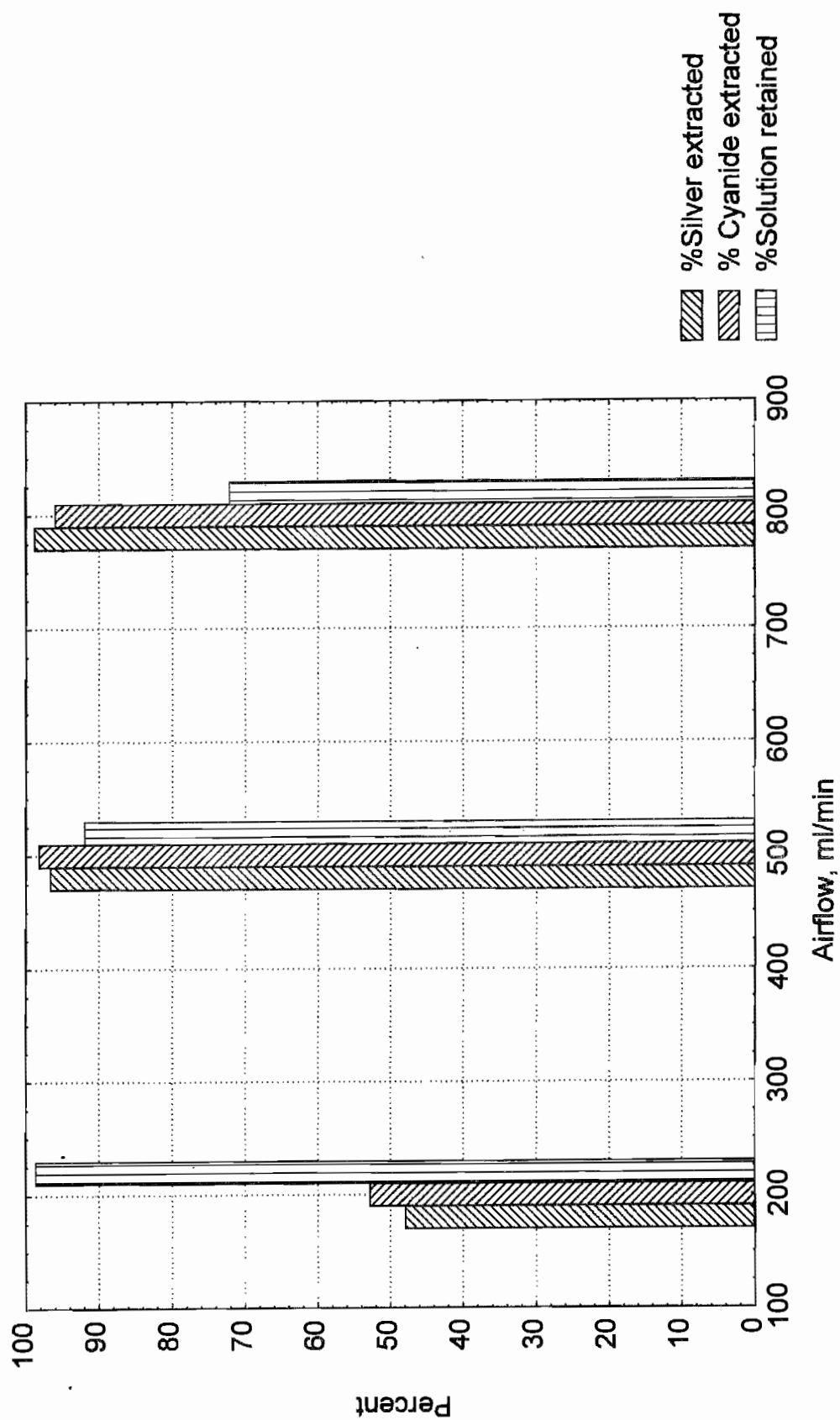


Figure 7
Effect of air flow on extraction, 1.0 g surfactant, 3 L batch cell.